About the bond energies in upd layers and the stability of nanosize metal clusters on a foreign substrate

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There is the impression that the interpretation of the phenomenon of underpotential deposition of metals on foreign substrates is still under discussion. A phenomenoöogical approach was published by Gerischer, Kolb and Przasnyski [1] relating the upd potential to the work function, but this approach does not take into account the crystallographic surface structure. A quantummechanical explanation of the Gerischer/ Kolb/Przasnyski relationship based on the jellium model was suggested by Leiva and Schmickler [2]. Improved calculations by these authors as well as by Neckel et. al. [3] take also into account the crystallographic structure of the surface. A thermodynamic analysis was given by Budevski, Staikov and Lorenz [4].
In the present paper it will be shown that (with reasonable approximations) it is possible to determine the sublimation enthalpy $\Delta_{sub}H_{upd}$ from the underpotential deposition (upd) potential. The analysis extends the Budevski/Staikov/Lorenz analysis and is based on the construction of a Nernst cell between a metal in the upd form and in the bulk form (Fig.1). The cell voltage of this cell is related (after some reasonable approximations) to the formation enthalpy of the upd form from the bulk state. The formation enthalpy is equal to the difference of the sublimation enthalpies as shown by a Born-Haber cycle. The following equation is obtained:

$$zF\Delta E_{upd} = \Delta_{sub}H_{upd} - \Delta_{sub}H_{bulk}$$

with $\Delta_{sub}H_{bulk}$ the sublimation enthalpy of the upd metal in its bulk form, and ΔE_{upd} the difference of the upd deposition potential (the peak maximum of the characteristic first main upd peak) and the Nernst potential of the bulk metal.
The value of the sublimation enthalpy can be used to calculate bond energies $\phi_{1/2}$ of upd metal atoms in positions comparable to kink sites following the equation [5]:

$$\varphi_{1/2} = \frac{\Delta_{sub}H_{upd}}{N_A} + \frac{1}{2}kT$$

This energy consists of the bond energies between the upd atoms and the substrate atoms and, depending on the lattice structure of the upd layer, bond energies between upd atoms itself.
In examples taken from the literature a surprising good correlation between the experimental values and model values is obtained.
On the basis of these results the stability of nanosize metal clusters of upd metals, (as deposited by the STM technique) is discussed.

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[4] E.Budevski, G.Staikov, W.Lorenz, Electrochemical phase formation and growth, VCH Verlagsgesellschaft, Weinheim 1996.
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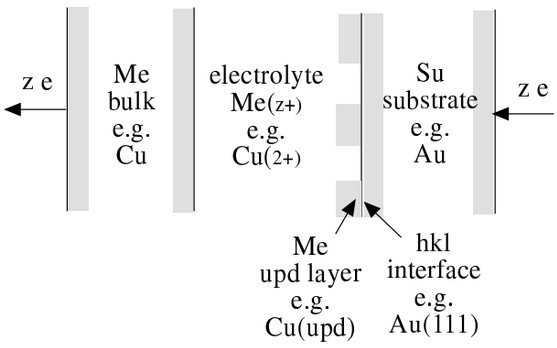

Fig.1 A Nernst cell used to analyse upd potentials.